

Theoretical study of the electronic structure of the $\text{Si}_3\text{N}_4(0001)$ surface

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Abstract

Density functional theory has been applied to a study of the electronic structure of the ideally-terminated, relaxed and H-saturated (0001) surfaces of $\beta\text{-Si}_3\text{N}_4$ and to that of the bulk material. For the bulk, the lattice constants and atom positions and the valence band density of states are all in good agreement with experimental results. A band gap of 6.7 eV is found which is in fair accord with the experimental value of 5.1–5.3 eV for H-free Si_3N_4 . Using a two-dimensionally-periodic slab model, a π -bonding interaction is found between threefold-coordinated Si and two-fold-coordinated N atoms in the surface plane leading to π and π^* surface-state bands in the gap. A surface-state band derived from s-orbitals is also found in the gap between the upper and lower parts of the valence band. Relaxation results in displacements of surface and first-underlayer atoms and to a stronger π -bonding interaction which increases the π – π^* gap. The relaxed surface shows no occupied surface states above the valence band maximum, in agreement with recent photoemission data for a thin Si_3N_4 film. The π^* band, however, remains well below the conduction band minimum (but well above the Fermi level). Adsorbing H at all dangling-bond sites on the ideally-terminated surface and then relaxing the surface and first underlayer leads to smaller, but still finite, displacements in comparison to the clean relaxed surface. This surface is more stable, by about 3.67 eV per H, than the clean relaxed surface.

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1. Introduction

Silicon nitride (Si_3N_4) is an important electronic material for use as a gate insulator and a diffusion barrier in integrated circuits and as a protective

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coating for magnetic storage devices. In contrast to the situation for other such materials, the surface electronic structure of Si_3N_4 is not well understood and appears to depend on the details of how the nitride is formed. For example, ultraviolet photoemission spectroscopy (UPS) data for a $\text{Si}(111)-(7 \times 7)$ surface nitrified by reaction with NH_3 at high temperature [1] show a surface state at 1.1 eV above the valence band maximum (VBM). On the other hand, a disordered (polycrystalline) Si_3N_4 film, grown on $\text{Si}(100)$ by low-pressure chemical vapor deposition and chemically cleaned in situ in ultrahigh vacuum (UHV), shows no evidence of surface states near the VBM [2]. As noted elsewhere [2] the vibrational spectrum of a Si surface nitrified by reaction with NH_3 is also markedly different from that of bulk Si_3N_4 . Charge trapping at Si_3N_4 surfaces, which may be defect-related, is a further important but not well-understood aspect of this material¹ [Refs. [3–6] and works cited]. One reason for the lack of information about atomically-clean and stoichiometric surfaces of bulk Si_3N_4 is the fact that a procedure for preparing such surfaces in UHV has only recently been reported [2].

The bulk electronic structure of Si_3N_4 has been studied extensively [7–17] using theoretical methods, and many groups have performed computational studies of either the chemisorption of atomic N [18–20] or the initial decomposition of NH_3 (e.g., Refs. [21–27]) on Si surfaces. However, less such work has been reported for the surfaces of bulk Si_3N_4 . Bagatur'yants et al. [28] performed an ab initio (RHF/MP2) cluster study of chemical reactions that occur on the $\beta\text{-Si}_3\text{N}_4(0001)$ surface during growth by chemical vapor deposition. In particular, relaxation of the clean surface was found to produce $>\text{Si}=\text{N}-$ structures as a means of eliminating dangling orbitals on the ideally-terminated surface (see below). Zhao and Bachlechner [11] considered α - and $\beta\text{-Si}_3\text{N}_4$ and found that Si–N bonds are more covalent on the unrelaxed surfaces than in the bulk.

In this work we will examine the physical and electronic structure of the ideally-terminated, the relaxed and the H-saturated $\beta\text{-Si}_3\text{N}_4(0001)$ surface using a two-dimensionally-periodic slab model in an ab initio density functional theory (DFT) calculation. This will allow the surface band structure to be obtained, which is not provided in a treatment of an isolated cluster. The results will also provide an understanding of the nature of the $\beta\text{-Si}_3\text{N}_4(0001)$ surface states which have not been addressed in detail previously.

2. Computational details

All calculations, except where noted, were performed using the CRYSTAL2003 suite of programs [29,30] which uses Bloch functions constructed from localized Gaussian basis sets. The Si basis set was the 65-111G* set developed by D'Arco et al. [31] for partially-ionic Si compounds, with the exponents of the outer sp- and d-shells re-optimized for Si_3N_4 . The results were 1.249, 0.5477 and 0.2834 for the sp-shells and 0.5437 for the d-shell (all in units of bohr^{-2}). The N basis set was the same 7-311G* set used for GaN [32], with exponents of the outer sp- and d-shells re-optimized for Si_3N_4 . The results were 0.4302 and 0.1357 for the sp-shells and 0.5976 for the d-shell.

Optimization of the basis sets and the unit-cell lattice constants was done using the LoptCG script² which computes gradients numerically using CRYSTAL98, followed by the application of a conjugate-gradient algorithm to locate the total-energy minimum. Optimization of the positions of individual atoms in the unit cell or on the surface were done using CRYSTAL2003 which obtains energy gradients analytically. The DFT calculations used the hybrid B3LYP functional which has been shown [33,34] to provide more

¹ The recurring reference to “ Si_3Ni_4 ”, instead of “ Si_3N_4 ”, in Ref. [6] is a misprint.

² The LoptCG script was obtained at <http://www.crystal.unito.it/>. At present, the publicly-available version of the script works only with CRYSTAL98. The latest version, CRYSTAL2003, can generate gradients analytically but only for the positions of individual atoms, not for basis-set parameters or lattice constants.

accurate band gaps than do purely *ab initio* functionals. The exchange–correlation potential was determined by numerical integration [29] rather than by fitting with Gaussian functions [35] as was done in CRYSTAL98. Due to the presence of singly-occupied dangling orbitals on the ideally-terminated (0001) surface (see below), spin-unrestricted DFT was used in all calculations involving clean surfaces. Si 3p (N 2p) electrons on surface sites with dangling orbitals were arbitrarily assigned initial spins of +1/2 (−1/2) to start the first self-consistent field (SCF) cycle. A shrinking factor of six was used for all reciprocal-lattice vectors in the **k**-point interpolations.

3. Results and discussion

3.1. Bulk properties

The physical and electronic structure of the bulk were analyzed as a necessary preliminary to addressing surface-related issues. For bulk β - Si_3N_4 the $P6_3/m$ structure (space group no. 176) was used [8,9], as shown in Fig. 1. The lattice constants and atomic positions were optimized as described above, and the results (Table 1) are found to be in good accord with experimental values [36] and with previous theoretical values.

Fig. 2 shows the computed VB density of states (DOS) together with results from UPS [2] and from X-ray photoemission spectroscopy (XPS) [37,38] for H-free Si_3N_4 . The orbital composition

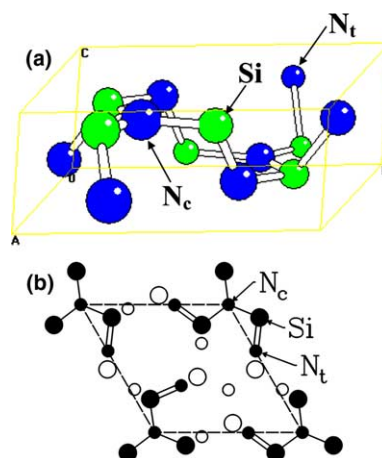


Fig. 1. (a) Unit cell for the bulk $P6_3/m$ lattice structure of β - Si_3N_4 , with atoms labelled as in Ref. [28]. (b) The ideal (unrelaxed) surface viewed along the surface normal. Solid (open) symbols refer to surface (first-underlayer) atoms, and the various inequivalent atom types are labelled. Bonds are shown between surface atoms, with double lines indicating the π -bonds that form when relaxation occurs. For clarity, bonds involving underlayer atoms are not shown. The unit-cell edges are shown in both panels.

of the various parts of the VB, which will be important in the following discussion of surface states, has been analyzed previously [14–16]. The lower part of the VB (from about −19 to −22 eV in Fig. 2) consists mainly of N s-orbitals with a small contribution from Si s-orbitals. In the upper part of the VB, states near the VBM arise mainly from non-bonding N p-orbitals oriented perpendicular to the plane of the N–Si–N bond, while

Table 1
Observed and calculated lattice parameters for β - Si_3N_4 ($P6_3/m$ structure)

Reference	Lattice constant (Å)		Si(6h) ^a		N2(6h) ^a	
	<i>a</i>	<i>c</i>	<i>x</i>	<i>y</i>	<i>x</i>	<i>y</i>
This work ^b	7.655	2.918	0.1738	0.7679	0.3303	0.0299
Ref. [7] ^b	7.6473	2.9171	0.1751	0.7689	0.3302	0.0307
Ref. [9] ^b	7.562	2.893	0.1741	0.7677	0.3302	0.0298
Ref. [10] ^b	7.622	2.910				
Ref. [15] ^b	7.61	2.91				
Ref. [36] ^c	7.608	2.911	0.1733	0.7694	0.3323	0.0314

^a The N1(2c) coordinates were fixed at $x = 1/3$, $y = 2/3$. The z -coordinate for all atoms was fixed at $z = 1/4$. Here “ x ” and “ y ” are fractions of the lattice constant “ a ”, and “ z ” is a fraction of “ c ”.

^b Theoretical results. See references for details of the calculations.

^c Experimental results.

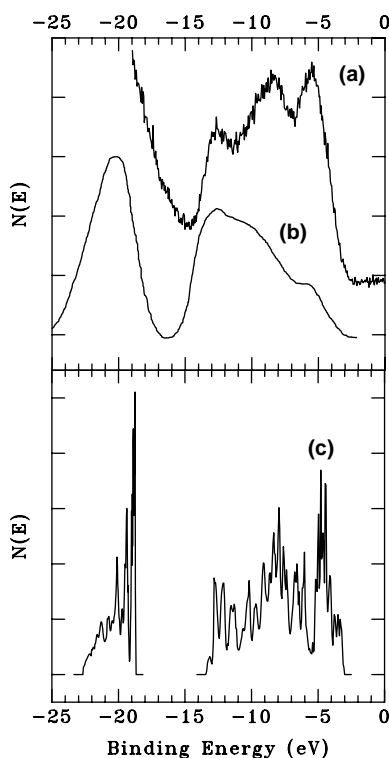


Fig. 2. Comparison of photoemission data with the calculated VB DOS for bulk β - Si_3N_4 . (a) HeII UPS ($h\nu = 40.8$ eV) from Ref. [2]. (b) MgK α XPS ($h\nu = 1253.6$ eV) from Ref. [38]. (c) Calculated VB DOS (this work). For all plots, binding energy is referenced to the calculated Fermi-level position, which falls near mid-gap. The UPS and XPS data were shifted in energy to align the peak near -13 eV with the corresponding feature in the calculated DOS.

deeper-lying states are due to Si–N σ -bonding orbitals. The bottom of the upper part of the VB (near -13 eV in Fig. 2) is derived largely from Si s-orbitals.

The width and overall shape of the DOS agree well with experiment, as do the results of previous calculations. The different appearance of the upper part of the VB in UPS and in XPS results from the increase in the relative photoionization cross-section for s- vs. p-orbitals at higher incident photon energies [39]. One notes in particular the close similarity between the UPS results, which were obtained for an atomically-clean polycrystalline surface under conditions of high surface sensitivity [2], and the corresponding bulk DOS of crystalline

β - Si_3N_4 . This supports the previous conclusion regarding the absence of surface states above the VBM for the Si_3N_4 samples discussed in Ref. [2]. Finally, a band gap of 6.7 eV was found in the present calculation vs. the experimental value of 5.1–5.3 eV reported [40–42] for H-free Si_3N_4 . As noted elsewhere [33], use of the B3LYP functional typically leads to a band gap that is somewhat larger than the experimental result.

3.2. The clean (0001) surface

3.2.1. The ideally-terminated surface

The surface was modeled using a two-dimensionally periodic slab which was six layers thick. Six layers are equivalent to three unit cells (cf. Fig. 1) stacked along the c -axis. This is sufficiently thick that no surface-related features appeared in the VB partial density of states (PDOS) for the middle of the slab and that the Mulliken charges on atoms in the middle of the slab were virtually the same as for the bulk material. Thus, six layers was considered to be sufficient to separate the two slab surfaces from each other. Since the present work uses localized, rather than plane-wave, basis sets it is not necessary to have periodically-repeated slabs along the surface normal.

Referring to Fig. 1, three Si and four N atoms lie in the ideally-terminated surface plane. Three of the N's ("terminal", labelled " N_t " as in Ref. [28]) are bonded to only two Si's, one in the surface plane and one in the first underlayer. Therefore, each N_t has a dangling orbital (in addition to the doubly-occupied non-bonding lone-pair orbital). The fourth N ("central", labelled " N_c ") is bonded to three Si's in the surface plane and thus has no singly-occupied dangling orbital. All three surface Si's are bonded to only three N's, and each has one dangling orbital. In the present calculations, the dangling bonds on the identical "back" surface of the slab were all terminated with H atoms, for which the standard Pople 6-31G** basis set was used.

In qualitative agreement with previous results [11], the Si– N_t bond on the ideally-terminated surface is found to be somewhat less ionic than in the bulk. The present results give +1.99 (-1.47) for the partial charge on a surface Si(N_t) atom vs. +2.15

(−1.63) for the corresponding bulk values. On the other hand, and also in accord with Ref. [11], the partial charge on a surface N_c atom (−1.59) is almost identical to that of a bulk N_c (−1.56). The Mulliken population analysis also indicates a significant π -bonding interaction between surface Si and N_t sites, even in the absence of relaxation, which affects the structure of surface states on the ideally-terminated surface (see below). This interaction leads to a Si– N_t overlap population of 0.392 at the surface vs. a value of 0.271 in the bulk.

Figs. 3a and 4a show band-structure results which indicate the presence of surface states in the lower part of the VB as well as near the bulk VBM. The bulk VBM was determined by identifying the highest-energy band that is composed largely of orbitals centered on atoms not in the surface plane. For clarity, only states within a few eV of the band edges are included in Fig. 3. Examination of the DOS (not shown) indicates that the occupied surface states are derived mainly from the surface N_t , with a smaller contribution

from surface Si, and that the occupancies are somewhat different for “up” and “down” spins as expected for states with singly-occupied, dangling-bond character. The occupied states near the VBM have a π -bonding character. The corresponding π^* -antibonding states are seen at approximately mid-gap in Fig. 3a.

3.2.2. The relaxed (0001) surface

The cluster results of Bagatur'yants et al. [28] indicate that surface relaxation takes the form of π -bond formation between Si– N_t nearest-neighbors which eliminates singly-occupied dangling orbitals. In the present work, relaxation was treated by starting with the ideally-terminated surface and allowing atoms in the surface layer and the first underlayer to move freely during optimization. Relaxation was found to lower the total energy by 3.12 eV per (1×1) surface unit cell.

Table 2 summarizes the structural results which are in qualitative agreement with those of previous work [28]. Relaxation results in an inward (outward) displacement of surface Si(N_c) atoms and

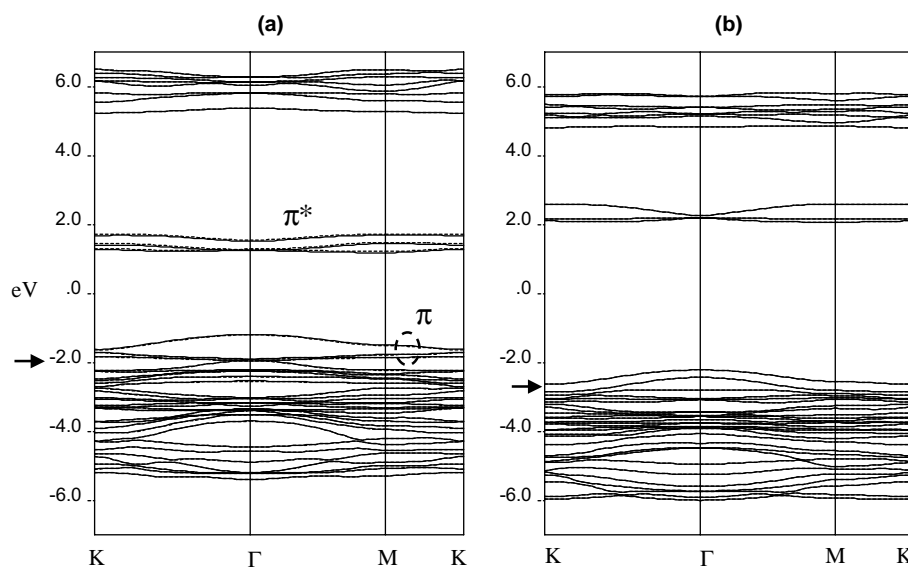


Fig. 3. Partial band structure diagram for (a) the ideally-terminated and (b) the relaxed β - $Si_3N_4(0001)$ surface for k -vectors in the plane of the two-dimensionally-periodic six-layer slab. The zero of energy is the Fermi level. States in the VB below about −5.5 eV and in the CB above about 6 eV are omitted (cf. Fig. 2). The arrows mark the approximate position of the “bulk” VBM (see text). The π and π^* surface-state bands involving surface Si and N_t sites are labeled in panel (a). For the π^* bands of panel (a), solid and dashed lines (barely distinguishable on the energy scale of the figure) show the “spin-up” and “spin-down” bands.

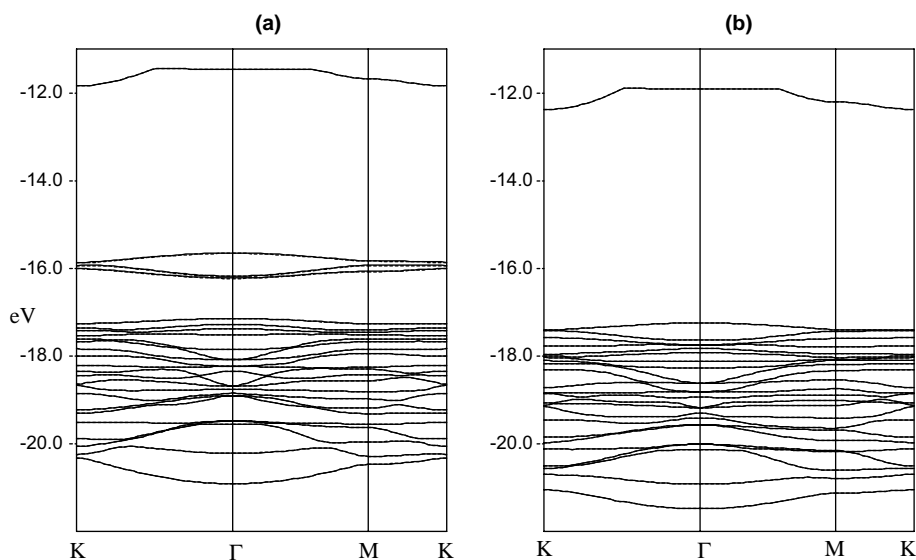


Fig. 4. Similar to Fig. 3 but showing the gap between the lower and upper parts of the VB (cf. Fig. 2). Valence states lying above -12 eV have been omitted for clarity.

Table 2

Structural parameters computed for the relaxed surface^a

	Si–N _c	Si=N _t	Si–N _t	N _t –Si	$\delta z(\text{Si})$	$\delta z(\text{N}_c)$	$\delta z(\text{N}_t)$
Surface	1.758	1.601	1.687 ^b	1.711 ^c	–0.16	+0.27	+0.02
First underlayer ^d	1.738			1.774	+0.08	+0.04	+0.02
Bulk	1.743			1.748			
Cluster [28] ^e	1.75	1.61			–0.24	+0.07	+0.10

^a All distances are in Ångströms. Si–N_c, etc. are bond lengths. The δz quantities are displacements along the surface normal relative to the atomic positions on the ideally-terminated surface. Omitted values are either not applicable or are zero by definition.

^b This is the back-bond distance between a surface Si and a first-underlayer N_t (cf. Fig. 1).

^c This is the back-bond distance between a surface N_t and a first-underlayer Si (cf. Fig. 1).

^d These distances refer to bonds within the first underlayer.

^e Results for the 3-DAS cluster model discussed in Ref. [28].

a slight outward displacement of the N_t, all of which are confined mainly to the surface layer. This results in the N_c atom lying about 0.43 Å above the plane of the three surface Si atoms to which it is bonded. In-plane (lateral) displacements of surface atoms occur mainly for the Si's, with a magnitude of about 0.22 Å. Those for the N atoms are small (~ 0.04 Å for N_t and ~ 0 for N_c). In contrast to the atomic positions, the atomic charges on the relaxed surface (+2.00, -1.41 and -1.49 for Si, N_t and N_c, respectively) are nearly the same as for the ideally-terminated surface (given above).

Formation of the Si=N_t π -bond is recognizable in the reduced interatomic distance (1.601 Å) and increased Mulliken overlap population (0.475) vs. the bulk Si–N_t σ -bond (1.748 Å and 0.271, respectively). The back-bonds from surface to underlayer atoms are also somewhat reduced in length and increased in overlap population in comparison to bulk bonds. On the other hand, the Si–N_t σ -bond within the first underlayer is slightly weakened (i.e., lengthened).

The surface core-level shift (SCLS) in binding energy (BE) for the N 1s and Si 2p levels at differ-

Table 3

Relative binding energy shifts calculated for the N 1s and Si 2p core levels for different forms of the $\text{Si}_3\text{N}_4(0001)$ surface^a

	Relaxed		Ideally-term.		H-saturated	
	N 1s	Si 2p	N 1s	Si 2p	N 1s	Si 2p
N _t bulk	0		0		0	
N _c bulk ^b	−0.47		−0.44		−0.34	
N _t surface	−0.87		−0.73		+0.26	
N _c surface	+1.68		+1.31		−0.14	
Si bulk		0		0		0
Si surface ^c		+0.68		+0.52		−0.27

^a All quantities are in eV, relative to either N_t bulk or Si 2p bulk. Negative (positive) values indicate a decrease (increase) in BE.^b The slightly different N_c bulk values reflect the level of precision in determining the BE shifts.^c A ~0.2 eV crystal field splitting of the clean-surface Si 2p is neglected.

ent sites was estimated for comparison with X-ray photoemission spectroscopy (XPS) results [2]. This was done simply by using the relative orbital energies for different inequivalent atomic species. Such an “initial-state” (Koopman’s theorem) approach neglects differences in core-hole screening [43] but should yield reasonable results for SCLSs (as opposed to absolute BEs). Table 3 summarizes the results. The Si and N_t SCLS values exhibit the trend expected [43] for partially-ionic materials in which cation (anion) core levels shift to higher (lower) BE due to the decrease in the number of oppositely-charged nearest-neighbor sites at the surface vs. in the bulk. The N_t SCLS is too small to be detected in the data presented in Ref. [2] given the limited instrumental resolution and surface sensitivity and the N 1s line width. It is noted that core-level line widths in partially-ionic materials such as Si_3N_4 receive a significant contribution from zero-point lattice vibration [44] in addition to the effects of any sample imperfections. Likewise, the estimated +0.68 eV shift for the surface Si 2p was not resolved [2] in the Zr M ζ -excited ($h\nu = 151.6$ eV) Si 2p XPS data. In this case, the instrumental resolution and surface sensitivity were much better than in the N 1s data, and a shift of this magnitude should have been observable. The results suggest that the magnitude of the SCLS is overestimated in Table 3, at least for the Si 2p.

A substantial shift to *higher* BE is found for the N_c 1s level at the relaxed surface. Relative to the bulk N_t, which contributes most of the N 1s intensity for MgK α excitation ($h\nu = 1253.6$ eV), the sur-

face N_c 1s is shifted 1.68 eV to higher BE. This agrees well (perhaps fortuitously so) with a surface-related satellite observed [2] at 1.7 eV below the main N 1s XPS peak for clean Si_3N_4 surfaces.³ Each N_c on the relaxed surface is in a configuration that can be depicted (cf. Fig. 1b) as N_c(−Si=N_t−)₃, and the large positive SCLS appears to be correlated with the strength of the Si=N_t π -bond. The positive SCLS is greatest for the relaxed surface, smaller for the ideally-terminated surface and absent (i.e., a small negative SCLS) on the H-saturated surface (see below).

Figs. 3b and 4b show the band structure diagram for the relaxed surface. The surface states evident in Figs. 3a and 4a for ideal termination are modified by the relaxation, which increases the Si–N_t interaction and shifts the π -bonding states down in energy and the π^* -antibonding states farther up into the gap. The empty bands in Fig. 3 represent virtual states and cannot be related quantitatively to observed inter-band transitions. However, the results suggest that transitions at energies less than the bulk band gap should be observable in surface-sensitive electron energy loss spectroscopy. Such an excitation has been reported [2] at ~4.6 eV which might be related to

³ Recent work [45] has found an N 1s SCLS of 0.7 eV to higher BE for thin films prepared by plasma nitridation of a Si(111) surface. Since different methods were used to prepare the surfaces studied in Refs. [2,45], it is unknown whether the physical origin of the satellite is the same in both cases.

Table 4
Structural parameters computed for the H-saturated surface^a

	HSi–N _c	HSi–N _t H	HSi–N _t	HN _t –Si	δz(SiH)	δz(N _c)	δz(N _t H)
Surface	1.744	1.726	1.749 ^b	1.730 ^c	+0.02	+0.17	–0.04
First underlayer ^d	1.751			1.745	+0.02	+0.12	0.00
Bulk	1.743			1.748			
Cluster [28] ^e	1.76	1.74			–0.01	+0.07	+0.04

^a See Table 2, footnote (a). In the present table, the optimized Si–H and N_t–H distances are 1.469 and 1.013 Å, respectively.

^b This is the back-bond distance between a surface SiH and a first-underlayer N_t.

^c This is the back-bond distance between a surface N_tH and a first-underlayer Si.

^d These distances refer to bonds within the first underlayer. No H is present in this layer.

^e Results for the (3-DAS)H₆ model discussed in Ref. [28].

the $\pi \rightarrow \pi^*$ transition of the Si=N_t bond. In the region between the upper and lower parts of the VB (Fig. 4), relaxation shifts the surface states to a position a few tenths of an eV above the bulk maximum of the lower part of the VB.

3.3. The H-saturated (0001) surface

Next we consider the surface that results when the singly-occupied dangling bonds (three on Si atoms and three on N_t sites) on the ideally-terminated surface are “tied up” with H. In the geometry optimization, the positions of the six H adatoms and of the surface and first-underlayer atoms were allowed to vary freely. As in the case of the other calculations described above, the “back” surface of the slab was terminated by H atoms in fixed positions. The structural results given in Table 4 show that the interatomic distances for the H-saturated surface are much closer to the corresponding bulk values, and the δz values generally smaller, than was the case for the clean relaxed surface. As expected, the SCLS values for the H-saturated surface (Table 3) are much less than for either clean surface.

The energy difference, ΔE_H, between the (clean) relaxed and H-saturated surfaces is given by

$$E(\text{relax.}) + 6E(\text{H}) = E(\text{H-sat.}) + 3E_{\text{ZP}}(\text{Si-H}) \\ + 3E_{\text{ZP}}(\text{N-H}) + \Delta E_{\text{H}}$$

where $E(\text{relax.})$ and $E(\text{H-sat.})$ are the geometry-optimized total energies of the respective surfaces and $E(\text{H})$ is the energy of the free H atom. In this definition, a positive ΔE_H indicates an exothermic

process. The calculation uses H atoms, rather than molecular H₂, since it is standard practice for H chemisorption experiments on non-metals to be performed using a hot (~2000 K) tungsten filament to dissociate the H₂ molecules. The E_{ZP} terms are the zero-point vibrational energies of the Si–H and N–H bonds. Any changes in the normal modes of the slab itself that may result from adsorption are ignored in applying the zero-point corrections. For the basis set used here, $E(\text{H}) = -13.558$ eV (close to the experimental value of -13.606 eV), and $E_{\text{ZP}}(\text{Si-H}) = 0.130$ eV and $E_{\text{ZP}}(\text{N-H}) = 0.211$ eV based on spectroscopic data [2] for the bond-stretching normal modes. The final result is ΔE_H = +22.021 eV per surface unit cell, or an average of 3.67 eV per adsorbed H, which indicates a substantial stabilization vs. the clean relaxed surface. This can be compared with typical molecular Si–H and N–H bond energies of about 3.0 and 4.0 eV, respectively [46]. The stabilization probably derives in part from the reduction in strain that accompanies elimination of the Si=N_t π-bond, in which the Si is forced into an approximately planar, threefold-coordinated configuration.

4. Summary and conclusions

Density functional theory, with the B3LYP functional and all-electron Gaussian basis sets, has been applied to a determination of the electronic structure of the ideally-terminated, relaxed and H-saturated (0001) surfaces of β-Si₃N₄ as

well as to that of the bulk material. A two-dimensionally-periodic slab model was used for the surface calculations. The results are as follows.

- (1) For the bulk, the lattice constants and atom positions and the VB DOS are all in good agreement with experimental results. A band gap of 6.7 eV is found which is reasonably close to the experimental value of 5.1–5.3 eV for H-free Si_3N_4 .
- (2) For the ideally-terminated surface a π -bonding interaction is found between threefold-coordinated Si and twofold-coordinated N atoms in the surface plane leading to π and π^* surface-state bands in the gap. A surface-state band derived from s-orbitals is also found in the gap between the upper and lower parts of the VB.
- (3) Relaxation leads to displacements of surface and first-underlayer atoms and to a stronger π -bonding interaction which increases the π – π^* gap. The relaxed surface shows no occupied surface states above the VBM (in agreement with recent UPS data [2] for a thin Si_3N_4 film). The π^* band, however, remains well below the CBM (but well above the Fermi level) and might be the final state in a sub-band-gap excitation observed [2] in ELS.
- (4) A high-BE N 1s satellite seen in XPS is identified with the threefold-coordinated (N_c) site on the relaxed surface on the basis of a Koopman's-theorem estimate of the SCLS. This corresponds to an experimentally-observed N 1s satellite [2]. Smaller SCLSs are predicted for $\text{Si}2p$ and N_t1s and have not yet been detected experimentally.
- (5) Adsorbing H at all dangling-bond sites on the ideally-terminated surface and then relaxing the surface and first underlayer leads to smaller, but still finite, displacements in comparison to the bare surface. The hydrogenated surface is more stable, by about 3.67 eV per H, than the clean relaxed surface.

These results provide a structural model for the Si_3N_4 surface which will be useful as a starting point in interpreting data from chemisorption

experiments and in understanding the properties of defects on this surface.

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References

- [1] J.W. Kim, H.W. Yeom, *Phys. Rev. B* 67 (2003) 035304.
- [2] V.M. Bermudez, F.K. Perkins, *Appl. Surf. Sci.* 235 (2004) 406.
- [3] H. Takeuchi, T.-J. King, *J. Electrochem. Soc.* 151 (2004) H44.
- [4] M. Naich, G. Rosenman, Ya. Roizin, M. Molotskii, *Solid-State Electron.* 48 (2004) 477.
- [5] Y. Aya, A. Ando, S. Yamasaki, K. Wakisaka, *Jpn. J. Appl. Phys.* 42 (2003) L1321.
- [6] E. Lusky, Y. Shacham-Diamand, A. Shappir, I. Bloom, B. Eitan, *Appl. Phys. Lett.* 85 (2004) 669.
- [7] P. Kroll, M. Milko, *Z. Anorg. Allg. Chem.* 629 (2003) 1737.
- [8] R. Belkada, M. Kohyama, T. Shibayanagi, M. Naka, *Phys. Rev. B* 65 (2002) 092104.
- [9] R. Belkada, T. Shibayanagi, M. Naka, M. Kohyama, *J. Am. Ceram. Soc.* 83 (2000) 2449.
- [10] W.Y. Ching, L. Ouyang, J.D. Gale, *Phys. Rev. B* 61 (2000) 8696.
- [11] G.L. Zhao, M.E. Bachlechner, *Phys. Rev. B* 58 (1998) 1887.
- [12] F. De Brito Mota, J.F. Justo, A. Fazzio, *Int. J. Quant. Chem.* 70 (1998) 973.
- [13] V.A. Gritsenko, Yu.N. Novikov, Yu.N. Morokov, *Fiz. Tverd. Tela* 39 (1997) 1342, English trans.: *Phys. Solid State* 39 (1997) 1191.
- [14] Y.-N. Xu, W.Y. Ching, *Phys. Rev. B* 51 (1995) 17379.
- [15] A. Reyes-Serrato, D.H. Galván, I.L. Garzón, *Phys. Rev. B* 52 (1995) 6293.
- [16] A.Y. Liu, M.L. Cohen, *Phys. Rev. B* 41 (1990) 10727.
- [17] J. Robertson, *Philos. Mag.* B 44 (1981) 215.
- [18] Y. Widjaja, A. Heyman, C.B. Musgrave, *J. Phys. Chem. B* 106 (2002) 2643.
- [19] G.-M. Rignanese, A. Pasquarello, *Phys. Rev. B* 63 (2001) 075307.
- [20] S. Higai, T. Ohno, *Appl. Phys. Lett.* 82 (2003) 4044.
- [21] C. Mui, Y. Widjaja, J.K. Kang, C.B. Musgrave, *Surf. Sci.* 557 (2004) 159.

- [22] H.-J. Kim, J.-H. Cho, *Phys. Rev. B* 69 (2004) 233402.
- [23] X. Xu, S.-Y. Kang, T. Yamabe, *Chem. Eur. J.* 8 (2002) 5351.
- [24] X. Lu, X. Xu, N. Wang, Q. Zhang, M.C. Lin, *Chem. Phys. Lett.* 355 (2002) 365.
- [25] Y. Widjaja, C.B. Musgrave, *Phys. Rev. B* 64 (2001) 205303.
- [26] H. Ezzehar, Ph. Sonnet, C. Minot, L. Stauffer, *Surf. Sci.* 454–456 (2000) 358.
- [27] Z.-H. Loh, H. Chuan Kang, *J. Chem. Phys.* 112 (2000) 2444.
- [28] A.A. Bagatur'yants, K.P. Novoselov, A.A. Safonov, J.V. Cole, M. Stoker, A.A. Korkin, *Surf. Sci.* 486 (2001) 213.
- [29] V.R. Saunders et al., *CRYSTAL2003 User's Manual*, University of Torino, Torino, 2003.
- [30] C. Pisani, R. Dovesi, C. Roetti, *Hartree-Fock Ab Initio Treatment of Crystalline Systems*, Springer, Berlin, 1988.
- [31] Ph. D'Arco, G. Sandrone, R. Dovesi, R. Orlando, V.R. Saunders, *Phys. Chem. Miner.* 20 (1993) 407.
- [32] V.M. Bermudez, *Surf. Sci.* 565 (2004) 89.
- [33] J. Muscat, A. Wander, N.M. Harrison, *Chem. Phys. Lett.* 342 (2001) 397.
- [34] W.F. Perger, *Chem. Phys. Lett.* 368 (2003) 319.
- [35] M.D. Towler, A. Zupan, M. Causà, *Comput. Phys. Commun.* 98 (1996) 181.
- [36] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vol. 3, American Society for Metals, Metals Park, OH, 1985.
- [37] R. Nietubýć, E. Sobczak, O. Šipr, J. Vackář, A. Šimůnek, *J. Alloys Compds.* 286 (1999) 148.
- [38] C. Sénémaud, M. Driss-Khodja, A. Gheorghiu, S. Harel, G. Dufour, H. Roulet, *J. Appl. Phys.* 74 (1993) 5042.
- [39] I.M. Band, Yu.I. Kharitonov, M.B. Trzhaskovskaya, *At. Data Nucl. Data Tables* 23 (1979) 443.
- [40] J. Bauer, *Phys. Stat. Sol. A* 39 (1977) 411.
- [41] V.A. Gritsenko, A.V. Shaposhnikov, W.M. Kwok, H. Wong, G.M. Jidomirov, *Thin Solid Films* 437 (2003) 135.
- [42] N. Pic, A. Glachant, S. Nitsche, J.Y. Hoarau, D. Goguenheim, D. Vuillaume, A. Sibai, C. Chaneliere, *Solid-State Electron.* 45 (2001) 1265.
- [43] W.F. Egelhoff Jr., *Surf. Sci. Rep.* 6 (1987) 253.
- [44] V.M. Bermudez, J.P. Long, *Appl. Phys. Lett.* 66 (1995) 475.
- [45] A. Bahari, U. Robenhagen, P. Morgen, Z.S. Li, *Phys. Rev. B*, submitted for publication.
- [46] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, first ed., Wiley, New York, 1962.